

## WE CLAIM:

1. A method of nanolithography comprising:  
 providing a substrate;  
 providing a scanning probe microscope tip;  
 coating the tip with a patterning compound; and  
 using the coated tip to apply the compound to the substrate so as to produce a desired pattern.
2. The method of Claim 1 wherein the substrate is gold and the patterning compound is a protein or peptide or has the formula  $R_1SH$ ,  $R_1SSR_2$ ,  $R_1SR_2$ ,  $R_1SO_2H$ ,  $(R_1)_3P$ ,  $R_1NC$ ,  $R_1CN$ ,  $(R_1)_3N$ ,  $R_1COOH$ , or  $ArSH$ , wherein:  
 $R_1$  and  $R_2$  each has the formula  $X(CH_2)_n$  and, if a compound is substituted with both  $R_1$  and  $R_2$ , then  $R_1$  and  $R_2$  can be the same or different;  
 $n$  is 0-30;  
 $Ar$  is an aryl;  
 $X$  is  $-CH_3$ ,  $-CHCH_3$ ,  $-COOH$ ,  $-CO_2(CH_2)_mCH_3$ ,  $-OH$ ,  $-CH_2OH$ , ethylene glycol, hexa(ethylene glycol),  $-O(CH_2)_mCH_3$ ,  $-NH_2$ ,  $-NH(CH_2)_mNH_2$ , halogen, glucose, maltose, fullerene C60, a nucleic acid, a protein, or a ligand; and  
 $m$  is 0-30.
3. The method of Claim 2 wherein the patterning compound has the formula  $R_1SH$  or  $ArSH$ .
4. The method of Claim 3 wherein the patterning compound is propanedithiol, hexanedithiol, octanedithiol, n-hexadecanethiol, n-octadecanethiol, n-docosanethiol, 11-mercapto-1-undecanol, 16-mercapto-1-hexadecanoic acid,  $\alpha,\alpha'$ -p-xylyldithiol, 4,4'-biphenyldithiol, terphenyldithiol, or DNA-alkanethiol.
5. The method of Claim 1 wherein the substrate is aluminum, gallium arsenide or titanium dioxide and the patterning compound has the formula  $R_1SH$ , wherein:  
 $R_1$  has the formula  $X(CH_2)_n$ ;  
 $n$  is 0-30;

X is  $-\text{CH}_3$ ,  $-\text{CHCH}_3$ ,  $-\text{COOH}$ ,  $-\text{CO}_2(\text{CH}_2)_m\text{CH}_3$ ,  $-\text{OH}$ ,  $-\text{CH}_2\text{OH}$ , ethylene glycol, hexa(ethylene glycol),  $-\text{O}(\text{CH}_2)_m\text{CH}_3$ ,  $-\text{NH}_2$ ,  $-\text{NH}(\text{CH}_2)_m\text{NH}_2$ , halogen, glucose, maltose, fullerene C60, a nucleic acid, a protein, or a ligand; and

m is 0-30.

6. The method of Claim 5 wherein the patterning compound is 2-mercaptoacetic acid or n-octadecanethiol.

7. The method of Claim 1 wherein the substrate is silicon dioxide and the patterning compound is a protein or peptide or has the formula  $\text{R}_1\text{SH}$  or  $\text{R}_1\text{SiCl}_3$ , wherein:

$\text{R}_1$  has the formula  $\text{X}(\text{CH}_2)_n$ ;

n is 0-30;

X is  $-\text{CH}_3$ ,  $-\text{CHCH}_3$ ,  $-\text{COOH}$ ,  $-\text{CO}_2(\text{CH}_2)_m\text{CH}_3$ ,  $-\text{OH}$ ,  $-\text{CH}_2\text{OH}$ , ethylene glycol, hexa(ethylene glycol),  $-\text{O}(\text{CH}_2)_m\text{CH}_3$ ,  $-\text{NH}_2$ ,  $-\text{NH}(\text{CH}_2)_m\text{NH}_2$ , halogen, glucose, maltose, fullerene C60, a nucleic acid, a protein, or a ligand; and

m is 0-30.

8. The method of Claim 7 wherein the patterning compound is 16-mercapto-1-hexadecanoic acid, octadecyltrichlorosilane or 3-(2-aminoethylamino)propyltrimethoxysilane.

9. The method of Claim 1 wherein the substrate is oxidized gallium arsenide or silicon dioxide and the patterning compound is a silazane.

10. The method of Claim 1 wherein the tip is coated with the patterning compound by contacting the tip with a solution of the patterning compound one or more times.

11. The method of Claim 10 further comprising drying the tip each time it is removed from the solution of the patterning compound, and the dried tip is contacted with the substrate to produce the desired pattern.

12. The method of Claim 10 further comprising drying the tip each time it is removed from the solution of the patterning compound, except for the final time so that the tip is still wet when it is contacted with the substrate to produce the desired pattern.

13. The method of Claim 10 further comprising:  
rinsing the tip after it has been used to apply the pattern to the substrate;  
coating the tip with a different patterning compound; and  
contacting the coated tip with the substrate so that the patterning compound is applied to the substrate so as to produce a desired pattern.
14. The method of Claim 13 wherein the rinsing, coating and contacting steps are repeated using as many different patterning compounds as are needed to make the desired pattern(s).
15. The method of Claim 14 further comprising providing a positioning system for aligning one pattern with respect to the other pattern(s).
16. The method of Claim 1 wherein the patterning compound acts as an etching resist, and the method further comprises chemically etching the substrate.
17. The method of Claim 1 wherein a plurality of tips is provided.
18. The method of Claim 17 wherein each of the plurality of tips is coated with the same patterning compound.
19. The method of Claim 17 wherein the plurality of tips is coated with a plurality of patterning compounds.
20. The method of Claim 17 wherein each tip produces the same pattern as the other tip(s).
21. The method of Claim 20 wherein the plurality of tips comprises an imaging tip and at least one writing tip, and each writing tip produces the same pattern as the imaging tip.
22. The method of Claim 21 wherein all of the tips are coated with the same patterning compound.
23. The method of Claim 17 wherein at least one tip produces a pattern different than that produced by the other tip(s).
24. The method of Claim 17 further comprising providing a positioning system for aligning one pattern with respect to the other pattern(s).

25. The method of Claim 1 wherein the tip is coated with a first patterning compound and is used to apply the first patterning compound to some or all of a second patterning compound which has already been applied to the substrate, the second patterning compound being capable of reacting or stably combining with the first patterning compound.

26. The method of Claim 25 wherein the second patterning compound has been applied to the substrate by immersing the substrate in a solution of the compound.

27. The method of Claim 1 further comprising treating the tip before coating it with the patterning compound to enhance physisorption of the patterning compound.

28. The method of Claim 27 wherein the tip is coated with a thin solid adhesion layer to enhance physisorption of the patterning compound.

29. The method of Claim 28 wherein the tip is coated with titanium or chromium to form the thin solid adhesion layer.

30. The method of Claim 27 wherein the patterning compound is in an aqueous solution, and the tip is treated to make it hydrophilic in order to enhance physisorption of the patterning compound.

31. The method of Claim 1 wherein the pattern is an array of a plurality of discrete sample areas of a predetermined shape.

32. The method of Claim 31 wherein the predetermined shape is a dot or a line.

33. The method of Claim 31 wherein each of the sample areas comprises a chemical molecule, a mixture of chemical molecules, a biological molecule, or a mixture of biological molecules.

34. The method of Claim 31 wherein each of the sample areas comprises a type of microparticles or nanoparticles.

35. The method of Claim 31 wherein the array is a combinatorial array.

36. The method of Claim 31 wherein at least one dimension of each of the sample areas, other than depth, is less than 1  $\mu\text{m}$ .

37. The method of any one of Claims 1-36 wherein the tip is an atomic force microscope tip.

38. A substrate patterned by the method of any one of Claims 1-36.
39. A kit for nanolithography comprising:  
a container holding a patterning compound; and  
instructions directing that the patterning compound be used to coat a scanning probe microscope tip and that the coated tip be used to apply the patterning compound to a substrate so as to produce a desired pattern.
40. The kit of Claim 39 comprising a plurality of containers, each container holding a patterning compound.
41. The kit of Claim 39 or 40 further comprising one or more additional containers, each of these containers holding a rinsing solvent.
42. The kit of Claim 39 further comprising a scanning probe microscope tip.
43. The kit of Claim 42 wherein tip is an atomic force microscope tip.
44. The kit of Claim 39 further comprising a substrate.
45. A kit for nanolithography comprising:  
a scanning probe microscope tip coated with a patterning compound.
46. The kit of Claim 45 wherein tip is an atomic force microscope tip.
47. The kit of Claim 45 further comprising one or more containers, each container holding a patterning compound or a rinsing solvent.
48. The kit of Claim 45 further comprising a substrate.
49. The kit of Claim 44 or 48 wherein the substrate is gold, and the patterning compound is a protein or peptide or has the formula  $R_1SH$ ,  $R_1SSR_2$ ,  $R_1SR_2$ ,  $R_1SO_2H$ ,  $(R_1)_3P$ ,  $R_1NC$ ,  $R_1CN$ ,  $(R_1)_3N$ ,  $R_1COOH$ , or  $ArSH$ , wherein:  
 $R_1$  and  $R_2$  each has the formula  $X(CH_2)_n$  and, if a compound is substituted with both  $R_1$  and  $R_2$ , then  $R_1$  and  $R_2$  can be the same or different;  
 $n$  is 0-30;  
 $Ar$  is an aryl;  
 $X$  is  $-CH_3$ ,  $-CHCH_3$ ,  $-COOH$ ,  $-CO_2(CH_2)_mCH_3$ ,  $-OH$ ,  $-CH_2OH$ , ethylene glycol, hexa(ethylene glycol),  $-O(CH_2)_mCH_3$ ,  $-NH_2$ ,  $-NH(CH_2)_mNH_2$ , halogen, glucose, maltose,

fullerene C60, a nucleic acid, a protein, or a ligand; and

m is 0-30.

50. The kit of Claim 49 wherein the patterning compound has the formula  $R_1SH$  or  $ArSH$ .

51. The kit of Claim 50 wherein the patterning compound is propanedithiol, hexanedithiol, octanedithiol, n-hexadecanethiol, n-octadecanethiol, n-docosanethiol, 11-mercapto-1-undecanol, 16-mercapto-1-hexadecanoic acid,  $\alpha,\alpha'$ -p-xylyldithiol, 4,4'-biphenyldithiol, terphenyldithiol, or DNA-alkanethiol.

52. The kit of Claim 44 or 48 wherein the substrate is aluminum, gallium arsenide or titanium dioxide, and the patterning compound has the formula  $R_1SH$ , wherein:

$R_1$  has the formula  $X(CH_2)_n$ ;

n is 0-30;

X is  $-CH_3$ ,  $-CHCH_3$ ,  $-COOH$ ,  $-CO_2(CH_2)_mCH_3$ ,  $-OH$ ,  $-CH_2OH$ , ethylene glycol, hexa(ethylene glycol),  $-O(CH_2)_mCH_3$ ,  $-NH_2$ ,  $-NH(CH_2)_mNH_2$ , halogen, glucose, maltose, fullerene C60, a nucleic acid, a protein, or a ligand; and

m is 0-30.

53. The kit of Claim 52 wherein the patterning compound is 2-mercaptoacetic acid or n-octadecanethiol.

54. The kit of Claim 44 or 48 wherein the substrate is silicon dioxide, and the patterning compound is a protein or peptide or has the formula  $R_1SH$  or  $R_1SiCl_3$ , wherein:

$R_1$  has the formula  $X(CH_2)_n$ ;

n is 0-30;

X is  $-CH_3$ ,  $-CHCH_3$ ,  $-COOH$ ,  $-CO_2(CH_2)_mCH_3$ ,  $-OH$ ,  $-CH_2OH$ , ethylene glycol, hexa(ethylene glycol),  $-O(CH_2)_mCH_3$ ,  $-NH_2$ ,  $-NH(CH_2)_mNH_2$ , halogen, glucose, maltose, fullerene C60, a nucleic acid, a protein, or a ligand; and

m is 0-30.

55. The kit of Claim 54 wherein the patterning compound is 16-mercapto-1-hexadecanoic acid, octadecyltrichlorosilane or 3-(2-

aminoethylamino)propyltrimethoxysilane.

56. The kit of Claim 44 or 48 wherein the substrate is oxidized gallium arsenide or silicon dioxide and the patterning compound is a silazane.

57. An atomic force microscope adapted for performing nanolithography comprising:

a sample holder adapted for receiving and holding a substrate; and

at least one well holding a patterning compound, the well being positioned so that it will be adjacent the substrate when it is placed in the sample holder.

58. The microscope of Claim 57 comprising a plurality of wells, at least one well holding a patterning compound, the other well(s) holding a patterning compound or a rinsing solvent, the wells being positioned so that they will be adjacent the substrate when it is placed in the sample holder.

59. An atomic force microscope adapted for performing nanolithography comprising:

a plurality of scanning probe microscope tips; and

a tilt stage adapted for receiving and holding a sample holder, the sample holder being adapted for receiving and holding a substrate..

60. The microscope of Claim 59 wherein the plurality of scanning probe microscope tips comprises an imaging tip and at least one writing tip.

61. The microscope of Claim 59 further comprising a plurality of wells, each well holding a patterning compound or a rinsing solvent, the wells being positioned so that they are adjacent the substrate when it is placed in the sample holder.

62. The microscope of Claim 59 wherein at least one of the tips is coated with a patterning compound.

63. The microscope of Claim 62 further comprising a substrate in the sample holder and wherein at least one of tips is contacted with the substrate so that the patterning compound coated on the tip is applied to the substrate so as to produce a desired pattern.

64. The microscope of Claim 63 wherein the tilt stage is adjusted so that all of the

tips are contacted with the substrate simultaneously and each of them produces the same pattern.

65. The microscope of Claim 64 wherein the plurality of scanning probe microscope tips comprises an imaging tip and at least one writing tip, and each writing tip produces the same pattern as the imaging tip.

66. The microscope of Claim 63 wherein the tilt stage is adjusted so that each of the plurality of tips is contacted separately with the substrate so that each tip produces a separate desired pattern.

67. The microscope of any one of Claims 59-66 wherein the tips are atomic force microscope tips.

68. A submicrometer array comprising:  
a plurality of discrete sample areas arranged in a pattern on a substrate,  
each sample area being a predetermined shape,  
at least one dimension of each of the sample areas, other than depth, being less than 1  $\mu\text{m}$ .

69. The array of Claim 68 wherein the predetermined shape is a dot or a line.

70. The array of Claim 68 wherein each sample area comprises a biological molecule, a mixture of biological molecules, a chemical molecule, or a mixture of chemical molecules.

71. The array of Claim 68 wherein each sample area comprises a type of microparticles or nanoparticles.

72. The array of any one of Claims 68-71 wherein the array is a combinatorial array.

73. A method of performing atomic force microscope (AFM) imaging in air comprising:

providing an AFM tip;

contacting the AFM tip with a hydrophobic compound so that the AFM tip is coated with the hydrophobic compound, the hydrophobic compound being selected so that



AFM imaging using the coated AFM tip is improved compared to AFM imaging using the same tip which is uncoated; and

performing AFM imaging in air with the coated tip.

74. The method of Claim 73 wherein the hydrophobic compound has the formula  $R_4NH_2$  wherein:

$R_4$  is an alkyl of the formula  $CH_3(CH_2)_n$  or an aryl; and  
n is 0-30.

75. The method of Claim 74 wherein the hydrophobic compound is 1-dodecylamine.

76. An atomic force microscope (AFM) tip coated with a hydrophobic compound, the hydrophobic compound being selected so that AFM imaging performed in air using the coated AFM tip is improved compared to AFM imaging performed using the same tip which is uncoated.

77. The tip of Claim 76 which is coated with a hydrophobic compound having the formula  $R_4NH_2$  wherein:

$R_4$  is an alkyl of the formula  $CH_3(CH_2)_n$  or an aryl; and  
n is 0-30.

78. The tip of Claim 77 which is coated with 1-dodecylamine.

79. An apparatus for depositing a compound on a substrate, comprising:

a first data collection including geometric entity data for one or more geometric entities, wherein for a first of the geometric entities there is: a corresponding first portion of the first data collection, and a corresponding second data collection of values for identifying of at least one of: the compound, the substrate, one or more tips for depositing the compound on the substrate, and a force of contact of at least one of said tips to a surface of the substrate;

a drawing data provider for obtaining diffusion related information for use in drawing the first geometric entity when said drawing data provider is supplied with said second data collection;

a pattern translator for determining one or more drawing commands for drawing the

first geometric entity on the substrate, at least one of said drawing commands generated using at least one of: a first value related to a time for drawing at least a portion of the first geometric entity, and a second value related to a drawing speed for at least a portion of the first geometric entity;

wherein said at least of the first and second values are determined using (i) information obtained from the diffusion related information, (ii) first information obtained from the first portion, and (iii) second information obtained from the second data collection; a drawing system for drawing said first geometric entity on the substrate when provided with said one or more drawing commands, said drawing system including a drawing tip wherein, in response to at least one of said drawing commands, said drawing tip draws said first geometric entity having an extent of less than one hundred micrometers.

80. The apparatus of Claim 1, wherein said drawing information includes a diffusion constant.

81. The apparatus of Claim 1, wherein at least one of: said first value is indicative of a holding time, and said second value is indicative of drawing speed.

82. The apparatus of Claim 1 further including a computer aided design system for obtaining said first data collection.

83. The apparatus of Claim 1, wherein said drawing system includes a scanning probe microscope.

84. The apparatus of Claim 5, wherein said scanning probe microscope includes an atomic force microscope.

85. The apparatus of Claim 1, wherein said drawing data provider includes one of: a user interface wherein a user manually enters said drawing information, a database to which a query is input for obtaining said drawing information, and an interpolation system for interpolating said drawing information.

86. The apparatus of Claim 1, wherein said first entity has an extent in a range of approximately one nanometer to one hundred micrometers.

87. A method of depositing a compound on a substrate, comprising:

first obtaining a first data collection including: (i) first geometric entity data for a first geometric entity, and (ii) a corresponding second data collection of one or more values for identifying of at least one of: the compound, the substrate, one or more tips for depositing the compound on the substrate, and (iii) a force of contact of at least one of said tips to a surface of the substrate;

obtaining diffusion related information for use in drawing the first geometric entity;

determining one or more drawing commands for drawing the first geometric entity on the substrate, at least one of said drawing commands generated using at least one of: a first value related to a time for drawing at least a portion of the first geometric entity, and a second value related to a drawing speed for at least a portion of the first geometric entity;

wherein said at least one of the first and second values are determined using: (i) information obtained from the diffusion related information, (ii) first information obtained from the first portion, and (iii) second information obtained from the second data collection;

drawing said first geometric entity on the substrate when provided with said one or more drawing commands, wherein, in response to at least one of said drawing commands, a drawing tip draws said first geometric entity having an extent of less than one hundred micrometers.